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TRANSLATION

NEWS IN REGIONS OF ELECTROCHEMICAL SYNTHESIS OF OXIDIZERS

By

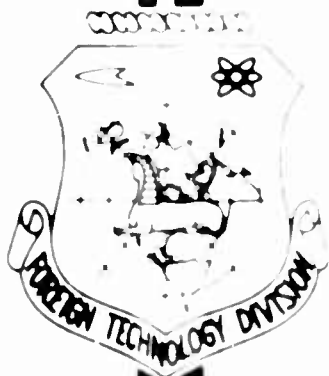
V. G. Khomyakov and M. Ya. Fioshin

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NEWS IN REGIONS OF ELECTROCHEMICAL SYNTHESIS OF OXIDIZERS

BY: V. G. Khomyakov and M. Ya. Fioshin

English Pages: 23

SOURCE: Khimicheskaya Promyshlennost', Nr. 1, 1962

S/063-062-000-001

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NEWS IN REGIONS OF ELECTROCHEMICAL SYNTHESIS OF OXIDIZERS

V. G. Khomyakov and M. Ya. Fioshin

Production of oxidizers is one of the most important branches of industrial electrochemistry. New works on electrosynthesis of oxidizers basically concern effective constructions of electrolyzers, improvements in flow charts, and also intensification of electrolysis process.

Oxygen Compounds of Chlorine

Majority of oxygen compounds of chlorine presenting technical interest are produced by electrochemical means.

In textile and paper industry, for bleaching sodium hypochlorite is widely used and for a long time many factories operated installations to obtain it by electrolysis of table salt. However, in connection with increase of production of liquid chlorine and appearance of new bleaching means [1] interest in electrochemical production of hypochlorite is lost, since it is significantly more expedient to obtain this product by chemical means from liquid chlorine and alkali. Data published recently on electrochemical synthesis of hypochlorite are not numerous [2-5]; they concern mechanism of anode processes [2] and constructions of electrolyzers of the filter-press type, producing small quantities of sodium hypochlorite for sterilization of water [4, 5], and also other types of electrolyzers [6].

Considerable work is carried out lately on electrochemical synthesis of

chlorates. Investigations were conducted for the purpose of more precise definition of conditions of electrolysis for achievement of optimum yield of product [7], improvement of flow sheet of production and development of new constructions of electrolyzers.

Much in this direction has been done by Japanese researchers [8-16]. It is established that reaction



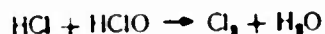
is reaction of first order [8], for which is derived equation of velocity constant [9]

$$K_1 = K \left(\frac{P_1}{P} \right)^2$$

where K — constant for reaction in absence of NaClO_3 ;

P and P_1 — vapor pressure of HClO in absence and in presence of NaClO_3 respectively.

During electrolysis of chlorides for the purpose of obtaining of chlorates, there occurs separation of a certain quantity of chlorine from the vat and for preservation of definite pH of the electrolyte it is necessary to introduce from 50 to 100 kg hydrochloric acid per 1 t of obtained sodium chlorate. Apparently, chlorine is lost due to reaction



and to evaporation of hyperchlorous acid. However, real losses exceed calculated [11]. Author (Imagava) considers that additional cause of losses of chlorine is leaks in vat.

There are interesting data in literature about distribution of products of electrolysis in reaction volume of chlorate electrolyzer [12].

There was studied corrosion of magnetite anode in chlorate electrolyzer [13], and also possibility of using for neutralization of alkalis not hydrochloric acid, but chlorine from waste gas [14].

A necessary condition in electrosynthesis of chlorate with high yield of

product is protection of hypochlorite and chlorate from reduction on cathode. This usually is attained by means of introduction into composition of electrolyte of small quantities of bichromate which will form on surfaces of the cathode a film, preventing penetration of ions of ClO^- and ClO_3^- and their electroreduction. However, this addition contaminates chlorate and elimination of it leads to large losses of product. A proposal to chrome-plate steel cathode [15] has been published, and is similar addition of bichromate indicated obtainable with this effect.

Obtaining of chlorate of potassium directly from salt water or carnallite has been reported [16]. For $\text{pH} = 2$, obtainable by means of acidification of salt water by hydrochloric acid, on carbon anode chlorate of potassium is obtained; however, product is strongly contaminated by sulfate of magnesium and sodium chloride. On steel cathode is precipitated hydroxide of magnesium, which does not occur during direct obtaining of chlorate of potassium by means of oxidation of 35% hydrous solution of carnallite.

Lately there have appeared descriptions of constructions of electrolyzers and flowsheets obtained on various foreign enterprises. Thus, for example, in [17], is given short description of constructions of 9 to 12 thousand amp electrolyzers. In other literature source are flowsheet and construction of 6-thousand amp electrolyzer used in India for production of chlorate [18].

Main efforts on improvement of constructions of chlorate electrolyzers are directed to increase of their productivity and lengthening of service life of anodes [19].

Construction of electrolyzer with revolving (2,500 - 3,000 rpm) graphite anode is proposed and certain results of test of semi-industrial model [20] are given. Authors indicate that this electrolyzer can operate during anode current densities up to $6,000 \text{ amp/m}^2$, volume concentrations to 64 amp/l and to obtain sodium chlorate with 78 - 84% current efficiency; expenditure of graphite here is 3 times less than is used on stationary anode, but expenditure of electric power is higher by 20 - 60%.

Significant attention is allotted the maintaining of thermal conditions of electrolyzers. For that are used cooling coils [21], and also hollow cooled anodes [17, 22]. For increase of service life of graphite anodes, it is proposed to impregnate them with artificial resins [15] or by linseed oil [23]. As is mentioned above, in order not to introduce bichromate into electrolyte, cathode is chrome-plated. To avoid reduction of anode products on cathodes it is recommended to prepare the latter from stainless steel [22] which turns out to be sufficiently effective. Attempts are made to obtain chlorates on anode of lead dioxide [24].

A number of improvements of flowsheet are proposed. For example, conditions are selected of obtaining of chlorate of potassium with minimum contents of impurities as a result of exchange reaction of sodium chlorate with chloride of potassium [25]. Flowsheet and conditions of electrolysis are developed, ensuring greatest transformation of hypochlorite into chlorate, lowered losses of chlorine and minimum current drain on yield of oxygen [21, 26].

There are interesting methods of synthesis of chlorates of alkali earth metals by direct oxidation of corresponding chlorides on anode. It is indicated [27] that during electrochemical oxidation of chloride of calcium it is expedient to use an amalgamated copper cathode, on which hydroxide film, hampering passage of current will be formed in smaller degree. In this case chlorate of calcium can be formed with current efficiency exceeding 70%.

Chlorate of magnesium it is possible to obtain by oxidation of chloride of magnesium [28]. It is expedient to use steel chrome-plated or tinned cathodes, from which film of hydroxide of magnesium is removed easier. Concentration of solution of chlorate of magnesium it is possible to bring to 400 - 500 g/l at 70% current efficiency.

Lately, the role of the compounds of chlorine — perchlorates richest in oxygen has grown, and its region of application has been expanded. Investigations of process of their electrochemical synthesis basically concerns attempts at replacement

of platinum anodes, introduction of certain changes in technological conditions and development of new constructions of electrolyzers. A steel electrolyzer for obtaining perchlorates, designed for 12 thousand amps and measuring 3,000 x 2,100 x 1,400 mm is described [17].

A slightly acid medium should be maintained in the electrolyte during electrosynthesis of perchlorates. If not salt, but perchloric acid is added for this purpose [29], then separation of chlorine on anode is eliminated, expenditure of acid is reduced by 10 times, pH is stabilized and content of bichromate can be decreased from 15 to 3 g/l.

The high potential with which occurs oxidation of chlorate into perchlorate limited the selection of material for manufacture of anode; only platinum was considered useful. However, lately there has appeared work on use in this process of anode of lead dioxide, deposited on base of nickel or tantalum [30, 32]. Here introduction of bichromate into electrolyte is not permissible, since it will form a film on surfaces of anode, thus lowering current yield of perchlorate. Instead of introduction of bichromate, it is recommended to use cathodes of steel— rust-resistant or nickel plated by chemical methods. Perchlorate of ammonium, obtained in such conditions from sodium perchlorate exchange reaction, possesses high degree of purity [31].

At 10,000 amp/m² current density on anode of dioxide of lead, in presence of 0.5 g/l sodium fluoride and at a temperature of 30 - 45° it is possible to receive sodium perchlorate with 91% current efficiency. It is reported [30] that anode of lead dioxide operated for 3,000 hours; here expenditure of electric power was 2.29 kWh per kg of sodium perchlorate with a final content of 30 g/l of sodium chlorate in electrolyte.

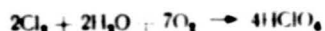
During use of anode from dioxide of lead, it is proposed [33] to conduct electrolysis to almost full exhaustion of electrolyte with respect to sodium chlorate. For that, for a fall of content of sodium chlorate in electrolyte be low 100 g/l,

it is recommended to introduce small quantities (to 10 g/l) of sodium persulfate. At 35° and anode current density of 3,000 amp/m², average current yield of sodium perchlorate is 73.3%, even when content of chlorate falls to 7.1 g/l.

It is noted that on new anodes from dioxide of lead, yield of perchlorates is lower, than on anodes, former in work [34].

Electrochemical method of obtaining of chloric acid presents significant interest. This acid it is possible to receive by chemical method from sodium perchlorate by treatment of concentrated hydrochloric acid.

Electrochemical method of synthesis of perchloric acid is based on oxidation of diluted hydrochloric acid on platinum anode [35]. Voltage on electrolyzer in this process is high due to low electrical conductivity of electrolyte [36], which however can be significantly increased by means of addition of sulfuric acid to hydrochloric acid. Now perchloric acid can be obtained with anode current yield of 48% at a current density of 2,000 amp/m², and temperature of 30°. Concentration of hydrochloric acid should not exceed [37] 0.006 N. It is proposed to subject to electrolysis a 25 - 40% solution of perchloric acid, precooled to 0° and saturated by chlorine [38]. Total reaction occurring here can be shown by equation



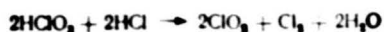
For a 2,000 - 3,000 amp/m² current density on platinum anode, it is possible to receive 60% HClO₄ of high degree of purity, containing in all 2 - 3 g/l chlorine. Current yield is nearly 70% at a total expenditure of electric power of 9 - 10 thousand kwh per 1 t of 100%-HClO₄.

Important bleaching oxygen compounds of chlorine are chlorine dioxide and sodium chlorite.

At present, in industries dioxide of chlorine is obtained by treatment of sodium chlorate by sulfuric acid [1]. As a result, chloric acid will be formed during whose decomposition dioxide of chlorine will be liberated. Methods are carried out also of obtaining dioxide of chlorine by reduction of sodium chlorate

by sulfurous gas, [1] or by treatment of chlorate by hydrochloric acid with subsequent use of the remaining later on removal of chlorine dioxide of solution in chlorate baths [39].

At one of English factories, dioxide of chlorine and sodium chlorite are obtained by electrochemical means [40]. For that process it is possible to use chloride-chlorate solutions, obtained in production of sodium chlorate [41]. Japanese researchers propose to receive dioxide of chlorine in a three-chamber electrolyzer, the central space of which is separated from anode by anion-exchange diaphragm, but from cathode, by a cationexchange diaphragm [42]. In central space is flooded solution of NaClO_3 , in anode — concentrated solution of chloric acid, and a solution of NaOH serves as catholyte. Porous graphite is used as anode, and cathode is prepared of steel. During electrolysis, hydrogen chloride is blown through anolyte or porous anode. Now reaction proceeds



In anode space ClO_2 containing 10% chlorine is continuously obtained. In cathode space is stored alkali, free from NaCl .

Instead of hydrogen chloride in anode space it is possible to give sulfur dioxide in quantity equivalent to quantity of chloric acid formed in anode space during electrolysis [43]. Reaction with sulfur dioxide can be expressed by equation



Role of electrolysis in given case consists in obtaining chloric acid in anode space. Method is convenient because simultaneously with dioxide of chlorine in cathode space will be formed alkali, but among products are absent sodium sulfate and table salt, stored during production of dioxide of chlorine by chemical method.

A number of methods of obtaining of dioxide of chlorine anticipates sodium chlorite as initial product. It is proposed to conduct oxidation of solution of sodium chlorite of 100 g/l in anode space on magnetite electrode [44].

Dioxide of chlorine is removed from anode space by insufflation by any inert gas.

Dioxide of chlorine obtained by electrochemical method sometimes contains significant impurity of chlorine which leads to undesirable processes of chlorination during use of ClO_2 as oxidiser. In order to avoid this electrochemical oxidation of sodium chlorite it is recommended to conduct process in presence of sodium sulfite [45]. Dioxide of chlorine, blown from anode space by inert gas contains in this case only traces of chlorine.

An interesting method [46] of obtaining of dioxide of chlorine from chlorite is in two electrolyzers, each of which is divided into two sections by a diaphragm from cation exchange resin. In anode space of first electrolyzer moves 25% solution of sodium chlorite. Electrolysis is conducted with graphite anode; in anode space will be formed dioxide of chlorine, being blown off by inert gas at a 5.5% ClO_2 concentration. Remaining solution, containing 15% NaClO_2 and 6.5% ClO_2 , will overflow into cathode space of second electrolyzer, where occurs reduction of dioxide of chlorine into chlorite. Then this solution is completely saturated by sodium chlorite and returns in anode space of first electrolyzer. Simultaneously in cathode space of first electrolyzer proceeds a weak solution of NaOH (4 g/l), where its concentration is increased to 10%. Then this solution will overflow into anode space of second electrolyzer and again returns into cathode space of first.

Dioxide of chlorine is a strong oxidiser, but it is impossible to transport it either in liquified or in compressed state due to great explosiveness. Therefore interest is developed to another oxidiser, sodium chlorite, which is transportable and is safe in circulation. Initial raw material for obtaining sodium chlorite by the chemical method is sodium chlorate which is reduced by sulfur dioxide, zinc, or sodium amalgam [1].

Attempts to receive chlorite by direct oxidation of sodium hypochlorite on various anodes did not have success [47]. Raw material for electrochemical synthesis

of chlorite is dioxide of chlorine.

For obtaining sodium chlorite a three-chamber electrolyzer is proposed. Central space of electrolyzer is separated from anode by a diaphragm of cation exchange resin and from cathode, by a diaphragm of anion exchange resin [48].

Chlorite will be formed in cathode space during electroreduction of dioxide of chlorine on graphite cathode. For that, in cathode space is flooded solution, containing 88.35% NaClO_2 , 7.21% NaClO_3 , and 4.44% NaCl . Central space is filled by a solution of NaClO_3 and anode, by a solution of NaOH . Through cathode space blows a mixture of dioxide of chlorine with air containing 6.5% ClO_2 . From central space solution enriched by sodium chlorite is brought out. Cathode current yield 80.4% at 62% utilization factor of ClO_2 .

It was also proposed to receive sodium chlorite by reduction of dioxide of chlorine in cathode space of dual chamber electrolyzer, separated from anode by diaphragm from cation exchange resin [49]. A solution of sodium chloride serves as anolyte. Initial catholyte contains 87% NaClO_2 , 6% NaClO_3 , 7% NaCl and is enriched during electrolysis to 96.3% NaClO_2 . Concentration of NaClO_3 accordingly falls to 3.3%, and NaCl -- to 0.4%.

Persulfuric Acid and Persulfate of Ammonium

These compounds are obtained only by electrochemical oxidation of sulfuric acid or bisulfate of ammonium. Main quantity of persulfuric acid and persulfate of ammonium goes to production of peroxide of hydrogen (by hydrolysis of these products is obtained ~80% of all peroxide of hydrogen [1, 17, 50]).

Large part of works published in literature recently concerning electrosynthesis of persulfates, is devoted mainly to new constructions of electrolyzers and mechanisms of anode processes.

Works on improvement of constructions of electrolyzers are conducted basically in direction of increase of anode and volume of current density, lowering of ohmic resistance of anodes, increase of effectiveness of cooling of electrolyte, and

replacement of platinum anodes.

There is described, for example 7,000 amp electrolyzer consisting of little separate cells connected in parallel [51, 52]. Electrolyte, fed into electrolyzer contains 500 g/l H_2SO_4 , and what flows from bath (with speed 0.9 l/min) contains 340 - 345 g/l. Current yield of persulfuric acid is 74 - 75%; temperature of electrolyte equals 19°; volume concentration of current is high and attains 1,000 - 2,000 amp/l; voltage to bath is 4.5 v. It is recommended to prepare anodes from metals which conduct current well, for example from aluminum or silver, coating them by a layer of platinum. In one cylindrical diaphragm it is possible to place bundle of anodes having form of narrow tapes.

Construction of electrolyzer in form of pipe in which cathode is made also in the form of long pipe is proposed. In center of latter is placed anode [53]. Electrodes are divided by diaphragm. Length of electrolyzer is calculated on attainment by electrolyte of a concentration (with respect to persulfuric acid) which allows immediate hydrolysis. There are proposals to cool anodes for decrease of decomposition of persulfate and increase of current efficiency. It is possible to cool, for example, by flooding low-boiling liquid [54] in a hollow anode. Cooling is achieved due to evaporation of liquid whose vapor heads for refrigerator and after condensation returns to internal cavity of anode in the form of liquid.

In other work there are data about dependence of yield of persulfate of ammonium on temperature of anode [55]. It is determined that yield of persulfate of ammonium is increased with decrease of temperature of anode, and its constant temperature it is increased with decrease of temperature of anolyte.

It is proposed to receive persulfate of ammonium in electrolyzer with revolving platinum anode [56]. For a 100,000 amp/m² anode current density current efficiency of persulfate of ammonium can attain 80%.

As anode, apparently, the appropriate form prepared dioxide of lead [57] is acceptable.

To lower cathode potential during electrosynthesis of persulfate of ammonium,

and consequently, to lower voltage on electrolyzer, it was proposed to replace lead-en cathode by a porous silver one [58].

Oxygen Compounds of Manganese

To a number of oxygen compounds of manganese, obtained by electrolytic means belongs permanganates of potassium and sodium, and dioxide of manganese.

There exist two industrial methods of obtaining permanganate of potassium -- oxidation of manganate of potassium or sodium on anode and anode dissolution of ferromanganese. Lately in literature more attention is given to the second method.

Works pertaining to first method have as a purpose increase of chemical stability of steel nickel plated anodes, for which before their use in electrolysis, they are subjected to thermal treatment at 300° for one hour, and then at 950 - 1,000° for 20 - 60 min. [59]. At 200 μ thickness of nickel coating, stability of heat treatment anodes approaches stability of nickel anodes. There are reported also conditions of obtaining permanganate of potassium of high purity from dilute solutions of manganate of potassium [60].

Method of obtaining permanganate by anode dissolution of metallic manganese or of its alloys was known long ago, but its realization is combined with a number of difficulties, the surmounting of which in significant degree has been managed only lately. During anode dissolution of pure metallic manganese in solutions of K_2CO_3 or KOH it is possible to obtain permanganate of potassium with 80 - 90% yield at an expenditure of electric power of 11 kWh per kg of product [61]. When using solutions of NaOH or Na_2CO_3 as electrolyte, anode dissolution of manganese accordingly leads to formation of sodium permanganate [62].

It is more expedient, however, to use as anode material not pure manganese, which is deficient, but ferromanganese, utilized in large quantities in metallurgy. Such attempts were begun repeatedly; however they clashed on one essential difficulty: during anode dissolution of ferromanganese in alkali solutions occurs passivation of anodes; on their surface appears film from dioxide of manganese and

eventually, process of dissolution is replaced by liberation of oxygen.

In the United States was process of electrochemical synthesis of sodium permanganate by anode dissolution of ferromanganese containing 80% Mn set up [17] on a small industrial scale. In approximately 24 hours of work, anode was passivated and process had to stop.

On the basis of works of R. I. Agladze with collaborators, in USSR there is organized industrial production of permanganate of potassium by anode dissolution of ferromanganese [63]. Process is carried out in solutions of K_2CO_3 (300 g/l) [64] or KOH (20%) [65] at a temperature of 16-18°. At an anode current density of 1,500 - 1,800 amp/m² in solutions of potassium carbonate, or, at 4,000 amp/m² in solutions of caustic potash, anodes from cast carbonic ferromanganese (71.18% Mn, 14.57% Fe, 6.47% C) are not passivated. Current efficiency is 40 - 45% according to substance -- 80 - 90% at an expenditure of electric power in carbonate solutions of 11 - 12 kWh per kg of permanganate, and in alkali -- 9 - 10 kWh per kg. Considerable works are devoted to the improvement of process of electrochemical obtaining of dioxide of manganese.

As it is known, dioxide of manganese in industries is produced by electrochemical oxidation of solutions of sulfate of manganese (100 g/l) in sulfuric acid (35 g/l) [1]. For a long time, lead was used as the anode. Lately anodes from graphite have become widely used. There is described [66] workshop in which are setup 33 electrolyzers (1,500 X 2,700 X 1,400 mm) with 600 graphite anodes in each; service life of anodes was 1 month. Initial anode current density was 100 amp/m²; load on bath was 7,000 - 9,000 amp; electrolysis is conducted at 90 - 94°; expenditure of electric power was 2.2 kWh for 1 kg MnO₂. Workshop gives 10 t MnO₂ in twenty-four hours.

There are published [67] proposals to conduct electrolysis of sulfate of manganese with graphite anodes in presence of small quantities of nitric acid. As anode, it is possible to use electrolytic dioxide of manganese, which is pressed on

current lead rod [68]. To obtain dioxide of manganese of high purity and not containing impurities C, Pb, Ni, and Co, it is recommended [69] to use titanic anodes and to work current densities of 100 - 200 amp/m². Passivation of titanic anode can be prevented by introduction of 0.5 - 0.4 g/l NaF into composition of electrolyte. Current efficiency for MnO₂ attain 75 - 90%. Removal of film of MnO₂ from surface of anode is possible by reversing current, by transmission of alternating current, or by transfer of anode into bath with sulfuric acid where during electrolysis film is removed by oxygen [70] which is being given off.

Additions of sodium fluoride show influence during use of PbO₂ or Pt as anode, increasing potential even in the presence of layer of MnO₂ on surfaces of anode and increasing current yield of dioxide of manganese [71]. Additions of sodium fluoride do not influence potential of graphite anode.

In patent literature [72] it is proposed to conduct electrolysis in bath with diaphragm from canvas or other filtering material and to use in anode space an electrolyte which contains, besides sulfate of manganese and sulfuric acid, an oxidizing - reducing addition [FeSO₄ + Fe₂(SO₄)₃]. Electrolyte continuously flows through diaphragm into cathode space. On cathode occurs partial reduction of Fe⁺⁺⁺ to Fe⁺⁺. Then from cathode space the electrolyte goes to tank with mixer, where pyrolusite is introduced. Under the influence of Fe⁺⁺ ions there occurs reduction of MnO₂ to MnO, which during reaction with sulfuric acid gives MnSO₄, directed to electrolysis.

There is developed also a method of obtaining dioxide of manganese from lean ores [73].

Bichromates

Bichromate is used in large quantities as oxidizer in organic chemistry. As a result of reactions of oxidation carried out in a sulfuric acid medium, sulfate of trivalent chromium is obtained. To oxidize the latter back into bichromate, and also to obtain bichromate by anode dissolution of ferrochrome, electrolysis is used.

Electrochemical regeneration of bichromate from worked solutions was used in industries long ago and had various constructive and technological resolutions.

In one of published works [74] there are defined optimum conditions of carrying out this process in bath without diaphragm and with diaphragm, using the example of regeneration of bichromate from industrial acid filtrates containing $\text{Cr}_2(\text{SO}_4)_3$ and H_2SO_4 . Essential problem during regeneration of bichromate is increase of stability of lead anodes. During anode polarization in solutions of sulfuric acid, surface of lead anode is covered by film of PbO_2 . However, this film is porous, and in solution there is always present organic compound, under whose influence the lead base of anode is destroyed [75]. Various methods of increase of stability of anode are proposed, in particular electrochemical precipitation of PbO_2 on perchlorvinyl fabric drawn across a lead pipe [76]. Such anodes remain in good condition even after six months of use, whereas the usual lead anodes serve for all of 3 weeks.

There is described cell for electrochemical oxidation of salts of chromium with horizontal diaphragm [77].

There are reported conditions of transformation of chromate into bichromate under the influence of electrolysis in electrolyzer with diaphragm [78].

Electrochemical obtaining of bichromate by anode dissolution of ferrochrome is recommended instead of multistage and insufficiently effective chemical method [79, 80]. To anode dissolution is subjected an alloy containing about 74.5% Cr, 22.0% Fe, 0.7% Si, and 2.7% C. A solution of NaOH (100 - 200 g/l) can serve as electrolyte. At a 400 - 600 amp/m² anode current density current yield of bichromate is 55 - 64%, and expenditure of electric power is 7 - 8 kWh per kg of bichromate. It is possible to work by combined method, i.e., to receive sodium chromate by the usual chemical method, and then to subject it to electrolysis using anodes of ferrochrome.

As electrolyte during anode dissolution of ferrochrome it is recommended to use also solution of NaCl and to receive sodium bichromate with 73% current

efficiency [81].

By anode dissolution of ferrochrome it is possible to receive bichromate of ammonium [82] and chromium anhydride [83]. The latter product is obtained also by means of electrochemical oxidation of chromium sulfate (prepared from chromite ore) on lead anode covered by dioxide of lead [84, 85].

Bromates, Iodate, and Iodic Acid

Lately in literature rather considerable attention is given to the electrochemical obtaining of bromates. There is a description of a small workshop started in Japan [86]. In workshop there are 24 steel electrolyzers setup, measuring 900 X 500 X 400 mm. Anodes were prepared from electrolytic lead dioxide, and the cathodes from stainless steel. It is stressed that use of graphite anodes worsens quality of bromate. The solution, containing 210 - 220 g/l KBr, 19 - 24 g/l KBrO_3 , and 2 g/l $\text{K}_2\text{Cr}_2\text{O}_7$ was electrolyzed. As a result of electrolysis at a 2,000 - 2,200 amp/ m^2 anode current density and temperature of 65 - 72° a solution containing 260 - 280 g/l KBrO_3 and 80 - 100 g/l KBr was formed. Current efficiency was 90 - 92%. Destruction of anodes was insignificant and constituted 57 - 60 g/t KBrO_3 .

At somewhat higher content of bromide of potassium, lower temperature and anode current density, it is possible to increase current yield of bromate of potassium to 98% [87].

In USSR technology of obtaining bromates of potassium and calcium is developed by M. N. Machulkin [88]. Author lists optimum conditions for electrosynthesis of bromates. To electrolysis is subjected a solution containing 280 g/l KBr, 2 g/l K_2CrO_4 . At a 600 amp/ m^2 anode current density, on graphite anodes there is a current efficiency of 92 - 95%. The means developed to increase stability of graphite anodes consisted in their impregnation by petroleum bitumen with subsequent firing at 350 - 400°.

In literature process of electrochemical synthesis iodic acid potassium on an industrial installation [89] is described. Oxidation of iodide of potassium is

produced on graphite anode at a 226 amp/m^2 current density and temperature of 50° . Here current efficiency reaches 94 - 96%. Electrolyzers with a capacity of 700 t are calculated on load of 500 amp.

There is considered also method of obtaining iodic acid by means of oxidation of solution of iodine in diluted hydrochloric acid on anode of lead dioxide [90]. During use of diaphragm which divides the cathode and anode space, and anode current density of $1,500 \text{ amp/m}^2$, it is possible to attain 95 - 99% current yield of product.

Perborate, Percarbonates, Tetra Acetate of Lead

Few new works are published on electrochemical synthesis of perborate. In literature there is information about electrolyzer on 7,000 amp for obtaining perborate [17]. In electrolyzer there are 21 platinum-iridium anodes and 22 cathodes of nickel-plated steels. Cooling is produced with the help of aluminum refrigerators, through which there circulates an aqueous solution of glycerine, cooled by ammonia. Cycle is continued 12 hours, after which from 1,200 t of electrolyte 240 kg perborate will be given off. Electrolysis is conducted at $11 - 12^\circ$ and anode current density is $1,500 - 2000 \text{ amp/m}^2$. Current efficiency is 57%, expenditure of electric power is 3.75 - 3.9 thousand kwh per t perborate.

By other data [91], perborate of potassium can be obtained by electrolysis of concentrated solutions of mixture of potash and borax at a $5,000 \text{ amp/m}^2$ current density on platinum anode, with current efficiency up to 93%. There are selected conditions for production of potassium percarbonate by oxidation of potash under high anode current densities [92].

Of other processes of electrochemical synthesis we will consider obtaining of tetra acetate of lead. This oxidizer possesses a number advantages as compared with PbO_2 , which is rather widely used in organic chemistry.

Electrochemical method of obtaining tetra acetate of lead is based on anode oxidation of diacetate of lead in glacial acetic acid on platinum anode [93, 94]. Electrolyte consists of solutions of 2.1 N $\text{Pb}(\text{CH}_3\text{COO})_2$ and 0.6 N CH_3COOK in

anhydrous acetic acid. Cathode and anode should be separated by diaphragm. With anode current density and cooling with water circulated through refrigerator, current yield of tetra acetate of lead is 95.5%. Product is obtained at a high degree of purity. Good results are attained on anode of PbO_2 [95].

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